Electro-organic Reactions, Part 10.† Mechanism of Anodic Cleavage of Dibenzyl Ether

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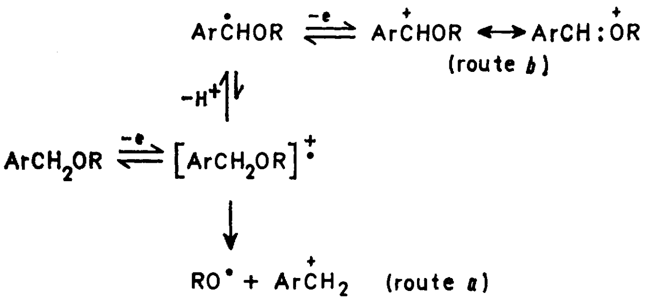
A detailed study of the voltammetry, coulometry, and products of the anodic oxidation in acetonitrile of dibenzyl ether suggests that, contrary to earlier reports, a one-electron oxidation occurs with the first-formed radical cation undergoing irreversible fragmentation. The subsequent chemical reactions are complex but a mechanistic scheme is presented which is consistent with the above and with additional experiments including an examination of the products of oxidation of dibenzyl [^{18}O]ether.

CLEAVAGE reactions are common at the cathode, where the first-formed radical anions may undergo rapid fragmentation into anions and radicals. At the anode a common fate of radical cations is rapid proton loss and further oxidation of the radicals so formed. Anodic cleavage may, however, be observed in cases where proton loss is difficult or precluded by structural factors. For instance, carbon–oxygen bonds may be anodically cleaved in 2,3,5,6-tetrasubstituted quinol diacetates [1] and in enol esters.[2] A carbon–carbon bond is cleaved in cyclopropanes [3], branched alkanes,[4] α-branched ketones,[5] and from diols.[6] The carbon–nitrogen bond is cleaved in aziridines,[7] and carbon–halogen bonds are cleaved relatively easily, although for the case of iodides it is not completely certain that the radical cation is the key intermediate.[8]

For the anodic cleavage of benzyl ethers the mechanism is not easily predicted. The relevant radical cation can lose a proton and be further oxidised, or split at a carbon–oxygen bond; in each case mesomerically stabilised cations are formed (Scheme 1). It has long been established that the benzyloxy function is electroactive.[9] On a preparative scale, anodic oxidation, in methanol, of *o*-, *m*-, and *p*-methyl- and *p*-methoxybenzyl methyl ethers gave the corresponding benzaldehydes in good yield.[10] This reaction has recently been developed as a method for removing *O*-benzyl protecting groups.[11]



SCHEME 1

In acetonitrile solution containing sodium carbonate exhaustive anodic oxidation of a number of benzylic alcohols, ethers and esters was reported [12,13] to give carbonyl compounds following the consumption [12] of up to 7 F mol^{-1}. In these studies it was also shown that, for the anodic conversion of diphenylmethyl dodecyl ether into benzophenone and dodecyl alcohol in the presence of $H_2{}^{18}O$, the ^{18}O was incorporated into the ketone but not into the alcohol.[13] Similar oxidation [13] of benzyl (−)-1-methylphenyl ether resulted in octan-2-ol in which configuration was retained. On this evidence Miller and his co-workers [12,13] favoured a mechanism involving proton loss following electron transfer (Scheme 1, route *b*). However, the results of the experiments based on ^{18}O labelling and retention of configuration do not allow a distinction between the alternative routes if route *a* involves, as is likely, formation of benzylic cations. The consumption of more than 1 F mol^{-1} is explained if the products are electroactive; indeed this must be so in some cases, *e.g.* the production of benzophenone from the initially formed diphenylmethanol.

Against this background we present the results of a detailed study of the coulometry, products, and voltammetry for the anodic oxidation in acetonitrile of dibenzyl ether.

RESULTS AND DISCUSSION

Products.—Because of possible complications caused by work-up procedures, analysis was carried out by g.l.c. following direct injection of samples of the anolyte. Anodic oxidation was typically performed in dried acetonitrile containing tetra-n-butylammonium perchlorate (0.5M) or sodium perchlorate (0.5M). Because of anode fouling a square wave pulse was imposed upon the anode; the brief pulse to 0 V removes the film of polymer.

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† Part 9, G. E. Hawkes, J. H. P. Utley, and G. B. Yates, *J.C.S. Perkin II*, 1976, 1709.

[1] (*a*) V. D. Parker, *Chem. Comm.*, 1969, 610; (*b*) J. H. P. Utley and G. B. Yates, *J.C.S. Chem. Comm.*, 1973, 473.

[2] T. Shono, Y. Matsumura, and Y. Nakagawa, *J. Amer. Chem. Soc.*, 1974, **96**, 3532.

[3] T. Shono, Y. Matsumura, and Y. Nakagawa, *J. Org. Chem.*, 1971, **36**, 1771.

[4] J. Y. Becker, L. L. Miller, and T. M. Siegel, *J.C.S. Chem. Comm.*, 1974, 341.

[5] J. Y. Becker, L. L. Miller, and T. M. Siegel, *J. Amer. Chem. Soc.*, 1975, **97**, 849.

[6] T. Shono, Y. Matsumura, T. Hashimoto, K. Hibino, H. Hamaguchi, and T. Aoki, *J. Amer. Chem. Soc.*, 1975, **97**, 2546.

[7] P. G. Gassman, I. Nishiguchi, and H. Yamamoto, *J. Amer. Chem. Soc.*, 1975, **97**, 1600.

[8] L. L. Miller and B. F. Watkins, *Tetrahedron Letters*, 1974, 4495.

[9] H. Lund, *Acta Chem. Scand.*, 1957, **11**, 491.

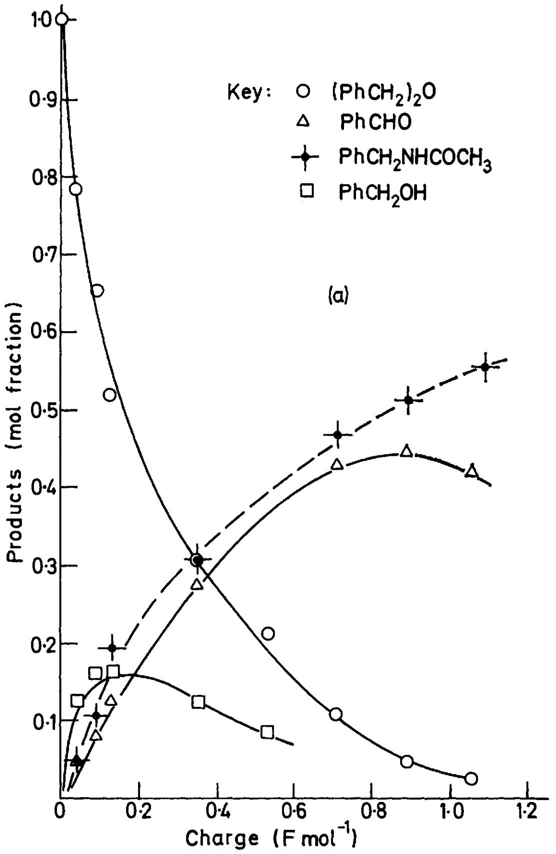
[10] R. F. Garwood, Naser-ud-Din, and B. C. L. Weedon, *Chem. Comm.*, 1968, 923.

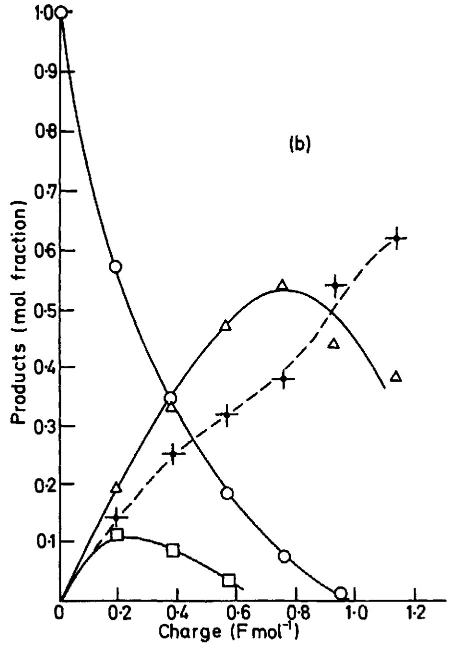
[11] S. M. Weinreb, G. A. Epling, R. Comi, and M. Reitano, *J. Org. Chem.*, 1975, **40**, 1356.

[12] L. L. Miller, J. F. Wolf, and E. A. Mayeda, *J. Amer. Chem. Soc.*, 1971, **93**, 3306.

[13] E. A. Mayeda, L. L. Miller, and J. F. Wolf, *J. Amer. Chem. Soc.*, 1972, **94**, 6812.

Products were identified by g.l.c. comparison with authentic samples. Quantitative analysis and the determination of material balances followed from the use of internal g.l.c. standards. The product distributions varied significantly with the extent of reaction and with the nature of the electrolyte. The results are presented graphically in Figure 1. The major features are: (i) the dibenzyl ether is largely consumed after the passage of 1 F mol^{-1} but the fall in concentration is not linear with charge; (ii) in acetonitrile [Figure 1(a)] and in acetonitrile containing trifluoroacetic acid [Figure 1(b)] the major products are *N*-benzylacetamide and benzaldehyde; (iii) in acetonitrile containing solid sodium carbonate formation of the amide appears to be somewhat suppressed; (iv) at low conversions benzyl alcohol is a relatively significant product but it remains at a low concentration as reaction proceeds.





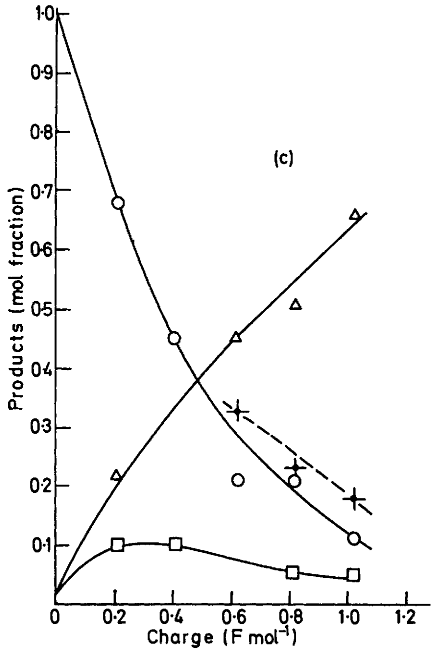


FIGURE 1 Products of dibenzyl ether oxidation: (a) MeCN–$Bu^n_4NClO_4$ (0.5M); (b) MeCN–$CF_3 \cdot CO_2H$ (10% v/v)–$NaClO_4$ (0.5M); (c) MeCN–$NaClO_4$–Na_2CO_3 (*ca.* 0.01 g cm^{-3} of anolyte)

It is also significant that, for electrolysis in acetonitrile, the production of amide and aldehyde reached a maximum at 1 F mol^{-1} and these were then apparently consumed until at about 2 F mol^{-1} the current fell rapidly. At this stage the anolyte was dark and viscous and from aqueous work-up only benzoic acid (0.7%) was isolated. Benzoic acid was reported [12,13] to be a major product of exhaustive electrolysis. In several electrolyses other minor products registered on g.l.c. but were not identified. The ether is stable for many hours in the presence of trifluoroacetic acid so it is likely that acid-catalysed conversion is slow.

Voltammetry and Coulometry.—Cyclic voltammetry at platinum or vitreous carbon of dibenzyl ether in acetonitrile, methylene chloride, or methylene chloride–trifluoroacetic acid (4 : 1 v/v) gave in each case irreversible oxidation peaks. The irreversibility was maintained at scan rates up to 30 V s^{-1} and the use of an asymmetric sweep (slow forward sweep, rapid reverse sweep) similarly failed to detect any reversibility. The peak shapes were broad [*cf.* ($E_p - E_{p/2}$) values in Table 1], but it is not clear whether the shape should in this case be attributed to contamination of the anode by filming, further oxidation of products, or slow, irreversible electron transfer. For the last possibility, theory predicts [14] $(E_p - E_{p/2}) = 48/\beta n$ mV, and the observed values of *ca.* 100 mV fit well for $\beta = 0.5$ and $n = 1$. The voltammetric results are summarised in Table 1.

TABLE 1

Cyclic voltammetry [a] of substituted dibenzyl ethers

Ether	Solvent	E_p/V [b]	$(E_p - E_{p/2})$/mV
Dibenzyl	MeCN	1.9	100
	MeCN	1.7 [c]	*ca.* 120
	CH_2Cl_2	2.5 [c,d]	*ca.* 400
	CH_2Cl_2–CF_3·CO_2H (4 : 1 v/v)	1.85	*ca.* 200
Bis-(2,4,6-trimethylbenzyl)	MeCN	1.65	
Bis-(4-methoxybenzyl)	MeCN	1.1, 1.3 [e]	

[a] Pt bead, 0.5M-tetra-n-butylammonium perchlorate, 0.3 V s^{-1}. [b] *vs.* Ag/Ag+. [c] Vitreous carbon anode. [d] *vs.* Ag wire. [e] 0.1 V s^{-1}.

From the shift in peak potentials (E_p) for oxidation of the two nuclear-substituted dibenzyl ethers it appears convenient to regard electron transfer as occurring from the aromatic ring rather than the oxygen atom. This is in line with earlier observations.[13]

Peak currents were linearly dependent on dibenzyl ether concentration (C) and the linearity was independent of sweep rate although absolute values of peak currents (i_p) increased with sweep rate (v). The variation of the current function, $i_p/Cv^{\frac{1}{2}}$, with sweep rate is shown in Figure 2. The shape of the curve is, according to theory,[15] that predicted for an ECE process and is similar to that found for the oxidation of triphenylamines.[16] At fast sweep rates the effect of the chemical step is minimised and the overall behaviour tends to be controlled by the initial electron-transfer step. At low sweep speeds there is time for oxidisable product to be formed at the microelectrode which, upon oxidation, causes the current function to increase. Peak potentials shift anodically with increasing sweep rate (Figure 3) and this is also consistent with an ECE process.

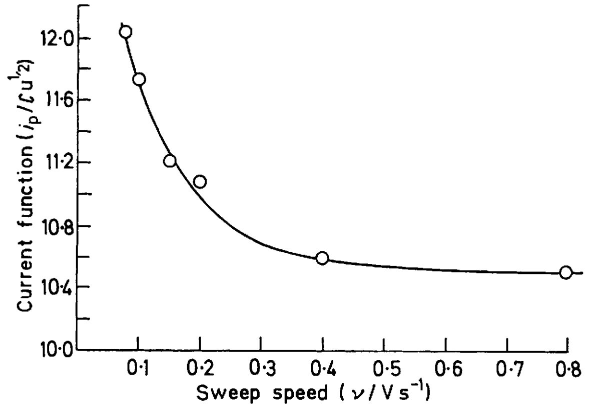


FIGURE 2 Variation of current function with sweep speed for dibenzyl ether [Pt bead, MeCN–$Bu^n_4ClO_4$ (0.25M), ref. Ag/Ag+]

The dependence of peak current on concentration was used to estimate n, the number of electrons transferred per mol in the interval of the voltammetric experiment. In these experiments the voltammetric response of dibenzyl ether was compared at a series of concentrations with that of ferrocene, which is known to give reversible electron transfer with $n = 1$. Because of the uncertainty associated with using for an irreversible process expressions based on the Randles–Sevcik equation (which holds for reversible reaction), the method was tested against 9,10-diphenylanthracene (DPA) which gives [17] two one-electron oxidation peaks, the first reversible and the second irreversible. It was found that for the second peak of DPA the expression for peak current which holds for slow electron transfer,[18] when combined with the use of the Randles–Sevcik equation for the ferrocene peak current, allowed a calculation of $n = 1$. Using the Randles–Sevcik equation for both ferrocene and DPA gave $n = 0.9$ for the DPA second oxidation peak. Application of the method to dibenzyl ether oxidation at a sweep rate of 0.3 V s^{-1} gave $n = 2.4$. Details are given in the Experimental section. Another assumption in this technique is that the diffusion coefficients of substrate and standard are similar. However, the results suggest either that dibenzyl ether is oxidised in a 2 F mol^{-1} process or that oxidation of the products contributes to the peak currents. To test the latter point the voltammetric peak potentials were measured for known and possible products and it is clear that they are all electroactive at the potential for dibenzyl ether oxidation (Table 2).

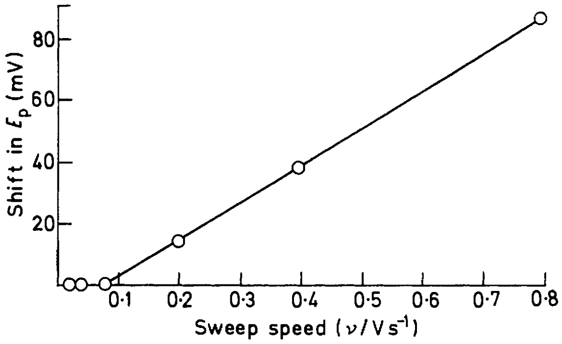


FIGURE 3 Variation of E_p with sweep speed for dibenzyl ether [Pt bead, MeCN–$Bu^n_4ClO_4$ (0.25M), ref. Ag/Ag+]

Mechanistic Rationalisation.—Many of the observations outlined above are new and several are at variance with some earlier results.[12,13] First, the anodic oxidation in aprotic solvent of dibenzyl ether is not electrochemically simple. The ether is not consumed in direct

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[14] R. N. Adams and S. Piekarski in ' Techniques of Chemistry,' vol. 1, Part IIA, ed. A. Weissberger and B. W. Rossiter, Interscience, New York, 1971.

[15] R. S. Nicholson and I. Shain, *Analyt. Chem.*, 1965, **37**, 178.

[16] E. T. Seo, R. F. Nelson, J. M. Fritsch, L. S. Marcoux, D. W. Leedy, and R. N. Adams, *J. Amer. Chem. Soc.*, 1966, **88**, 3498.

[17] O. Hammerich and V. D. Parker, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1972, **38**, Appendix 9.

[18] P. Delahay, *J. Amer. Chem. Soc.*, 1953, **75**, 1190.

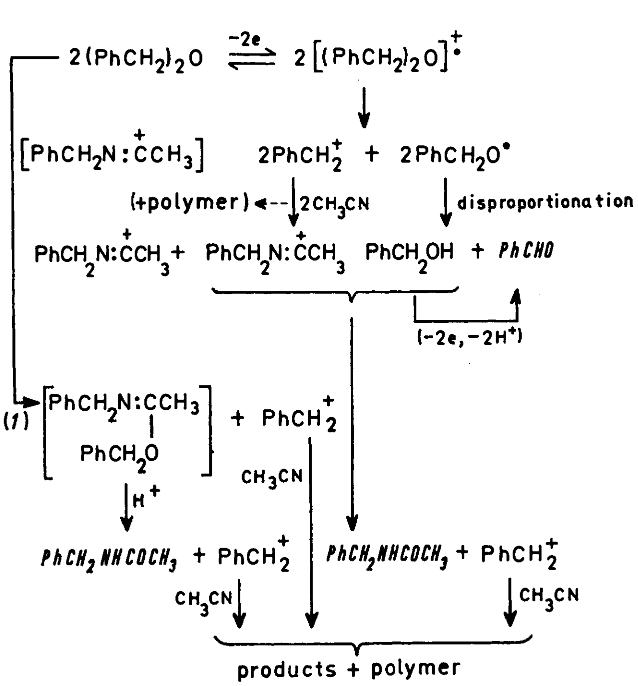
proportion to the charge passed. However, complete consumption of the ether requires 1 F mol^{-1} and not 2 F mol^{-1} as previously believed. Secondly, *N*-benzylacetamide is a major product and its formation is not restricted to oxidation in dry acetonitrile only.[13] Considerable amounts of the acetamide are formed in acetonitrile with and without Na_2CO_3, $CF_3{\cdot}CO_2H$, or H_2O-(5% v/v), and with either tetra-n-butylammonium perchlorate or sodium perchlorate as supporting electrolyte. Thirdly, the products are oxidised further at + 1.9 V; this is presumably the origin of the benzoic acid (33% yield after 4 F mol^{-1}) previously reported.[12] In our hands little benzoic acid was found and polymerisation appeared to be the main reaction after 1 F mol^{-1}.

TABLE 2

Cyclic voltammetry [a] of products

Compound	E_p/V(*vs.* Ag/Ag$^+$)
PhCHO	2.10
$PhCH_2{\cdot}OH$	1.86
$(PhCH_2)_2$	1.80
$PhCH_2{\cdot}NHAc$	1.86
$(PhCH_2)_2NAc$	1.86

[a] Pt bead, acetonitrile–tetra-n-butylammonium perchlorate (0.05M), 0.3 V s^{-1}; all oxidations irreversible.



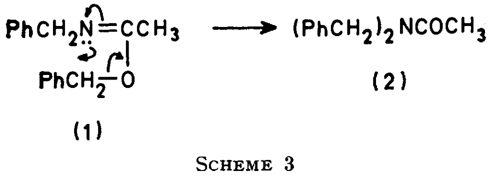
SCHEME 2

The coulometry, products, and complexity of the reaction are mostly reconciled in Scheme 2. The non-linear curves for the ether and the concentration profile for benzyl alcohol as reaction proceeds are consistent with their acting as nucleophiles. This point has been tested by using ^{18}O-labelled starting material (see below). Given that the relative extents of attack by the two nucleophiles on the nitrilium ion are unknown and may change with the extent of reaction, and that some polymerisation is also occurring, it is not likely that Scheme 2 is a complete representation of the mechanism. Its essential features are: (i) the ether is anodically cleaved in a one-electron process; (ii) benzaldehyde is a disproportionation product; and (iii) the intermediate nitrilium ion may be attacked by benzyl alcohol. The results of experiments designed to test these points are described below.

A precise interpretation of the stoicheiometry implied in Scheme 2 is obscured by the further oxidation of products (including oxidation of benzyl alcohol to benzaldehyde) and the consumption of dibenzyl ether by its attack on nitrilium ions. A simple interpretation of Scheme 2 predicts a maximum aldehyde:ether ratio of 0.5 : 1; from Figure 1 values of 0.43 (1a), 0.52 (1b), and 0.68 (1c) are obtained. Clearly the reaction in the presence of sodium carbonate (1c) differs from that in neutral or acidic solution; apart from the larger than expected amount of aldehyde the initially produced *N*-benzylacetamide is consumed electrochemically at an early stage in the reaction. In this case it may well be that two-electron oxidation predominates (Scheme 1, route *b*) and Scheme 2 does not apply.

Anodic Oxidation of Dibenzyl [^{18}O]*Ether*.—Dibenzyl ether enriched with ^{18}O (*ca.* 3%) was electrolysed in dry acetonitrile to 1 F mol^{-1} at 2.0 V and samples of benzaldehyde and *N*-benzylacetamide were isolated by preparative-scale g.l.c. For benzaldehyde, accurate mass measurement at *m/e* 107 confirmed the presence of $[PhC^{18}O]^+$ and for the amide the $(M + 2)$ peak was similarly located. Comparison of the peak heights with those for the corresponding ^{16}O-containing ions gave the ^{18}O enrichment as 3% for both products. The benzyl alcohol content of the anolyte was too small to be so analysed. A duplicate experiment confirmed these results. Within the precision of the method, therefore, the oxygen in the products comes from the ether and not, for instance, from adventitious water. The formation of labelled amide and benzaldehyde is well explained by initial cleavage of the dibenzyl ether radical cation.

Reaction of N-t-Butylacetonitrilium Hexachloroantimonate with Benzyl Alcohol.—The reaction between alcohols and nitrilium ions would be expected to yield isolable imidate esters.[19] Consequently electrolysis of dibenzyl ether according to Scheme 2 should give the benzyl imidate (1). However, attempts to prepare and characterise this compound resulted in the formation of *NN*-dibenzylacetamide (2), presumably due to the rearrangement shown in Scheme 3. The g.l.c. properties



SCHEME 3

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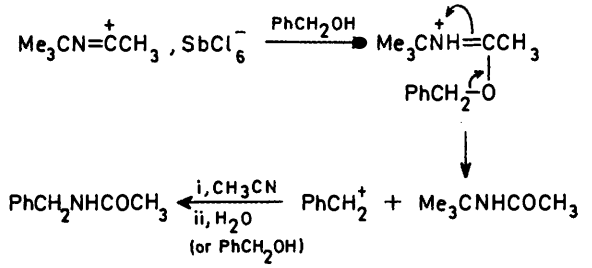
[19] H. Meerwein, P. Laasch, R. Mersch, and J. Spille, *Chem. Ber.*, 1956, **89**, 209.

of the diamide (2) were ascertained and it was shown to be absent from the electrolysis products, which suggests that the benzyl esters have an alternative mode of decomposition. This view was supported by an experiment involving a relatively stable nitrilium salt. *N*-t-Butylacetonitrilium hexachloroantimonate (3) was prepared and dissolved in benzyl alcohol–acetonitrile. Analysis, following aqueous work-up, showed the presence of *N*-t-butylacetamide and *N*-benzylacetamide in approximately equal quantities. This result is rationalised in Scheme 4, and it strongly supports the hypothesis for the mechanism of *N*-benzylacetamide formation in the electrolysis of dibenzyl ether. Miller and his coworkers [13] have suggested that the benzyl cation necessary for amide formation arises from the acid-catalysed dehydration of benzyl alcohol and they cite as evidence the increase in the amide : aldehyde ratio which results from addition of benzyl alcohol to a freshly electrolysed solution of dibenzyl ether in acetonitrile. Clearly their result is consistent with the anolyte containing *N*-benzylnitrilium ions rather than protons.



SCHEME 4

The Disproportionation Step: Anodic Oxidation of Sodium Benzyl Oxide.—There is good precedent for disproportionation of the benzyloxyl radical. In the presence of cobalt salts benzyl hydroperoxide is decomposed [20] in acetic acid to give benzaldehyde and benzyl alcohol. Furthermore, it is well established [21] that such disproportionation is highly exothermic with an enthalpy change of 350 kJ mol^{-1}. As part of the present study several attempts were made electrochemically to generate benzyloxyl radicals and to establish their fate under anodic conditions.

The first such experiment involved the electrolysis at +2.0 V of sodium benzyl oxide in acetonitrile containing lithium perchlorate (0.5M). The salt, which was isolated as a viscous liquid, not only occluded benzyl alcohol but was also sparingly soluble in acetonitrile. The salt suspension slowly dissolved during electrolysis and the cell current fell after the passage of 1 F mol^{-1}. Disproportionation requires the formation of equal quantities of aldehyde and alcohol. This was the case at low conversion but as reaction proceeded the ratio increased. This may be attributed to further oxidation of benzyl alcohol, known to be electroactive at +2.0 V. Such further oxidation has been observed before; diphenylmethanol produced from the corresponding dodecyl ether is oxidised [13] to benzophenone and from the anodic cleavage of benzyl *p*-methoxyphenyl ether no *p*-methoxybenzyl alcohol is produced,[11] presumably because it is oxidised further. Separate detailed studies of the electrochemical behaviour of both benzyl alcohol [22] and *p*-methoxybenzyl alcohol [23] have established that the alcohols are oxidised to the aldehyde at the potentials used for cleavage of the relevant ethers.

Because the rate of disproportionation is proportional to $[PhCH_2O\cdot]^2$ and competing abstraction to $[PhCH_2O\cdot]$ the ratio of aldehyde to alcohol should be influenced by current density. An electrolysis of dibenzyl ether was carried out at +1.7 V (where oxidation of alcohol should be diminished) and the initial current was about one tenth of that at +1.9 V. Under these conditions electrode filming was severe and it was only at low conversion that product ratios were consistent with a simple interpretation of Scheme 2. Assuming that attack on the nitrilium ion by ether is relatively insignificant, a ratio of aldehyde to amide of 1.0 : 1 is predicted; at 0.29 F mol^{-1} the ratio is 0.9 : 1.

The experiments designed to test the validity of the disproportionation step did not, therefore, give a clear-cut answer because the experimental difficulties and the complexity of the overall reaction embodied in Scheme 2 make interpretation at high conversions difficult. The product ratios at low conversion, however, support the Scheme.

EXPERIMENTAL

Materials.—*Solvents and supporting electrolytes.* Acetonitrile (Hopkin and Williams G.P.R.) was purified by a modification of Coetzee's method.[24] The solvent was stirred with calcium hydride (10 g l^{-1}) for 2 days, decanted, then fractionally distilled from phosphorus pentaoxide (5 g l^{-1}) by using a Vigreux column (1 m) with a 3 : 1 reflux ratio. The process was repeated and the final fraction (middle cut) collected and stored over molecular sieves (4 Å). For cyclic voltammetry one commercial product (Fluka; puriss.) gave good results following treatment with molecular sieves.

Sodium perchlorate (B.D.H. AnalaR; $NaClO_4,2H_2O$) was dried at 110 °C in a vacuum oven. Tetra-n-butylammonium perchlorate was prepared from the corresponding bromide [25] and dried at 100 °C under reduced pressure immediately before use.

Dibenzyl ether. This was prepared by the reaction between sodium benzyl oxide (formed in liquid ammonia) and benzyl bromide. It was purified by fractional distillation under reduced pressure; b.p. 157—159° at 10 mmHg.

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[20] Y. Takegami, Y. Fujimura, H. Ishii, and T. Iwamoto, *Kogo. Kagaku Zasshi*, 1965, **68**, 196 (*Chem. Abs.*, 1965, **63**, 14,663).

[21] P. Gray and A. Williams, *Chem. Rev.*, 1959, **59**, 239.

[22] O. R. Brown, S. Chandra, and J. A. Harrison, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1972, **38**, 185.

[23] O. R. Brown, S. Chandra, and J. A. Harrison, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1972, **34**, 505.

[24] J. F. Coatzee, G. P. Cunningham, D. K. McGuire, and G. R. Padmanabhan, *Analyt. Chem.*, 1962, **34**, 1139.

[25] H. O. House, E. Feng, and N. P. Reet, *J. Org. Chem.*, 1971, **36**, 2371.

4,4′-Dimethoxydibenzyl ether. To a solution of 4-methoxybenzyl alcohol (2.4 g, 0.017 mol) in dimethylamide–1,2-dimethoxyethane (50 cm^3; 2 : 1 v/v) was added 4-methoxybenzyl chloride (2.7 g, 0.017 mol) and the mixture was cooled to − 10 °C. Sodium hydride (0.3 g of 80% dispersion) was added during 8 min and the temperature allowed to rise to 60 °C. More sodium hydride (0.3 g) was added and the mixture stirred for 45 min, then poured into water (100 cm^3). The product was extracted with chloroform and worked up in the usual way. Fractional distillation gave a yellow liquid (3 g, 68%; b.p. 180—184° at 0.1 mmHg) which solidified. Recrystallisation (aqueous methanol) gave plates, m.p. 35—37° (lit.,[26] 39°).

Bis-(2,4,6-*trimethylbenzyl*) *ether.* 2,4,6-Trimethylbenzyl chloride was prepared from the corresponding acid with thionyl chloride; b.p. 106° at 20 mmHg. The acid chloride was converted into 2,4,6-trimethylbenzyl alcohol by reduction with lithium aluminium hydride in ether [m.p. 85—87° (lit.,[27] 88°)], and the alcohol was treated in benzene solution with phosphorus tribromide to give 2,4,6-trimethylbenzyl bromide [m.p. 58—59° (lit.,[28] 50—51°)]. 2,4,6-Trimethylbenzyl alcohol (1 g, 0.006 mol) in dry ether (20 cm^3) was added to sodium hydride (0.2 g; 80% dispersion) in dry ether (20 cm^3). An ethereal solution of 2,4,6-trimethylbenzyl bromide (1.2 g, 0.006 mol) was added and the mixture stirred for 2 days at room temperature. The product ether was isolated as a white solid (1.5 g, 88%), m.p. 116—120°, $\nu_{max.}$ (Nujol) 850 (ArH), 1 070 (C–O), and 1 460 cm^{-1} (C–CH$_3$); δ(CCl$_4$), 2.2 (6 H, s, ArCH$_3$), 2.25 (12 H, s, ArCH$_3$), 4.4 (4 H, s, ArCH$_2$·O), and 6.68 (4 H, s, ArH).

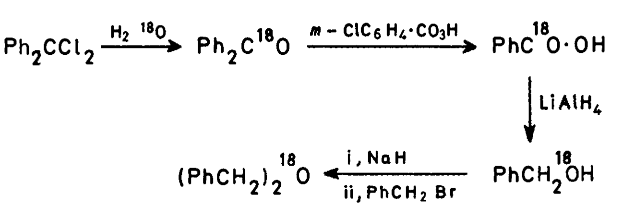
TABLE 3

Controlled-potential oxidation of dibenzyl ether

		Products (mol l^{-1})			
Charge [a]	PhCHO	PhCH$_2$·OH	PhCH$_2$·NHAc	(PhCH$_2$)$_2$O	Material balance (mol l^{-1}) [%]
0				0.208	0.208 [100]
0.19	0.039	0.022	0.028	0.117	0.206 [100]
0.38	0.058	0.014	0.043	0.059	0.174 [84]
0.57	0.087	0.006	0.059	0.034	0.186 [89]
0.76	0.113		0.080	0.015	0.208 [100]
0.95	0.09		0.110	0.003	0.203 [98]
1.14	0.08		0.130		0.210 [100]

[a] F mol^{-1} of dibenzyl ether.

Dibenzyl [^{18}O]*ether.* The standard reactions outlined in Scheme 5 were used to introduce the ^{18}O label. Water enriched in ^{18}O (3.34 atom %) was supplied by Prochem.



SCHEME 5

The final product was examined by mass spectrometry: *m/e* 200.109 (C$_{14}$H$_{14}$^{18}O requires 200.108 7), 109.054 (*M* − PhCH$_2$; C$_7$H$_7$^{18}O requires 109.053 9). Comparison of the peak heights for *m/e* 109 and 107 gave ^{18}O : ^{16}O as 0.03 : 1.

Electrochemical Experiments.—Apparatus. Conventional glass H-cells with sintered glass separators were used. For both preparative and voltammetric experiments suitable combinations of the following modules were used: Potentiostat (TR70/2A), Waveform Generator (RB1), and electronic current integrator (all Chemical Electronics Ltd.), together with an X–Y recorder (Hewlett–Packard 7035B) or oscilloscope (Telequipment D53A).

Coulometry. Cyclic voltammograms were recorded for a mixture of the substrate and ferrocene at several concentrations. Voltammetry was carried out at a platinum bead in acetonitrile or methylene chloride containing sodium perchlorate (0.5M) or tetra-n-butylammonium perchlorate (0.5M) and a sweep speed of 0.3 V s^{-1} was used. For methylene chloride solution a silver wire sufficed as a reference electrode and in acetonitrile the reference was Ag/AgClO$_4$ (0.1M). Plots of peak current *vs.* concentration were linear for substrate and ferrocene and from the relative slopes *n* values were calculated as described in the text.

Controlled potential oxidation of dibenzyl ether. In a typical experiment dibenzyl ether (1.08 g, 0.005 mol) was added to the anode compartment of an H-cell containing trifluoroacetic acid (10% v/v) in acetonitrile–sodium perchlorate (0.5M) (25 cm^3) and the solution was electrolysed at a platinum foil anode (area 1.32 cm^2). The anode potential was 2.0 V [*vs.* Ag/AgClO$_4$ (0.1M)], which was pulsed to 0 V for 0.6 s at 10 s intervals. Samples of the anolyte (typically 100 μl) were withdrawn at convenient coulomb intervals and added to pre-weighed amounts of internal standard (biphenyl). The samples were analysed directly by g.l.c. [Perkin-Elmer F11; column 2 m × 0.3 cm o.d., 8% Antarox CO990 on Chromosorb W, programmed at 180 °C (7 min) rising to 215 °C at 25 °C min^{-1}]. Three chromatograms were recorded and the average integrated peak areas were used in calculations of product distributions. The detector response factors were measured for each of the major products. Typical results are displayed in Table 3.

Controlled potential oxidation of dibenzyl [^{18}O]*ether.* Acetonitrile was twice distilled from phosphorus pentaoxide, collected over molecular sieves (4 Å) and siphoned into a dry flask containing a weighed amount of anhydrous sodium perchlorate. The solution was then siphoned into a carefully dried H-cell equipped as for the above-described electrolysis. The background current at 2.0 V was 151 μA cm^{-2}. Dibenzyl [^{18}O]ether (3% ^{18}O; 1.16 g) was added and electrolysed as described above. The reaction was terminated at 0.9 F mol^{-1} and samples of the anolyte were removed and subjected to preparative scale g.l.c. (Varian A-920; column 3 m × 0.6 cm o.d., 20% Antarox CO990 on Chromosorb, W, 180—215 °C). The fractions containing

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N-benzylacetamide and benzaldehyde were collected and examined by mass spectroscopy. For two such experiments the key results were: amide M^+ 151.089 and 151.088 (3% ^{18}O) ($C_9H_{11}N^{18}O$ requires 151.088 3); aldehyde $(M - 1)^+$ 107.038 and 107.038 (3% ^{18}O), ($C_7H_5{}^{18}O$ requires 107.038 2).

Controlled potential electrolysis of sodium benzyl oxide. Benzyl alcohol was added to a suspension of sodium hydride in dry ether. The ether and the excess of benzyl alcohol were removed under reduced pressure and a portion (0.15 g) of the yellow viscous residue was rapidly transferred to the anode compartment of an H-cell containing acetonitrile–lithium perchlorate (0.5M). The resulting suspension was electrolysed and the products were analysed as described for dibenzyl ether.

Preparative Experiments.—Attempted preparation of the imidate (1). Dry silver(I) oxide was prepared by mixing aqueous solutions (0.1M) of sodium hydroxide and silver nitrate and repeatedly washing the precipitate with water, then acetone and finally dry ether. The dry oxide (4.5 g, 0.02 mol), was added gradually to a solution of *N*-benzylacetamide (1.5 g, 0.01 mol) in benzyl bromide (15 cm^3). When the reaction had subsided benzene (20 cm^3) was added and the mixture heated under reflux for 3 h. After filtration and the removal under reduced pressure of benzene and benzyl bromide the product was isolated by t.l.c. [silica gel HF; acetone–light petroleum (b.p. 60—80 °C) (70% v/v)]. It was shown by i.r. and n.m.r. spectroscopy to be identical with an authentic sample of *NN*-dibenzylacetamide (2).

N-*t-Butylacetonitrilium hexachloroantimonate* (3) *and its reaction with benzyl alcohol.* The nitrilium salt was prepared by Meerwein's method [19] and divided into two portions each of 3 g. To the first was added saturated aqueous sodium hydrogen carbonate (30 cm^3) and the organic layer was extracted with ether (3 × 10 cm^3). Drying (Na_2SO_4) and removal of the ether gave *N*-t-butylacetamide (0.6 g, 73%), m.p. 97—99° (lit.,[29] 101—102°).

The second portion was added to a mixture of acetonitrile (1 cm^3) and benzyl alcohol (1 cm^3). The solution became dark red and after 2 h aqueous saturated sodium hydrogen carbonate was added. The organic products were extracted with ether and worked up as described above, and the residue was analysed by g.l.c. Major peaks of approximately equal area were identified as being due to *N*-t-butylacetamide and *N*-benzylacetamide.

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[6/888 *Received*, 10*th May*, 1976]

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